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**AERODYNAMIC LEVITATION REACTOR STUDIES OF
FLUORINE REACTIONS WITH REFRACTORY CERAMICS**

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I. INTRODUCTION

In recent years, much progress (1-4, 6-8, 17-19, 33, 34, 36-39, 50, 52-3, 58-71) has been made towards one goal of this (19, 33, 37-9, 50, 53, 61-6) and other (17, 18, 34, 36, 52, 59, 60) research: to survey heterogeneous fluorine reactions in different families of materials. The present work has, ~~therefore~~ placed a greater emphasis on our second goal, i.e., the detailed kinetic and mechanistic study of selected fluorine/ceramic reactions. The results of our program include work on fluorine reaction with Al_2O_3 (38, 39), B_4C (33, 37), Re (61, 64), Gd (61, 65), LaB_6 (37, 50, 61, 63) and LaB_6-C , LaB_6-MoSi_2 composites (61, 63).

One application of materials resistant to fluorine attack at high temperature is the HF chemical laser. Nickel and nickel alloys are useful in fluorine to ca. 1000K, but higher temperatures are required in CW HF lasers. Since the number of candidate materials decrease and fluorine corrosion rates increase with temperature it is useful to set upper bounds on the temperatures required for this application. Our analysis of this problem (61, 66) is presented, ~~in Section II below.~~

Given the temperature range of interest, the mechanisms by which fluorine gasifies solids limit the number of possible fluorine resistant materials. These are discussed also in Section II.

In Sections III - IX we summarize the experimental results of this program. These results have already been presented (19, 37-9, 50, 53, 59, 61-2). Here we present a brief discussion of the essential results, along with abstracts of the papers that have been prepared for publication.

The list of references included here is a bibliography of work in the area of heterogeneous fluorine gas/solid reaction kinetics along with the additional references used in preparing this and previous reports. Titles are included to assist the interested reviewer of this subject.

II. TEMPERATURE REQUIREMENTS AND CORROSION RATES IN EFFICIENT HF SUPERSONIC DIFFUSION LASERS (66)

Abstract - Design parameters for a $(D_2 + F_2)$ combustion driven HF supersonic diffusion laser include the temperatures and pressures in the laser cavity (T, P) and the combustor (T_0, P_0), the choked half width, w^* , of the supersonic expansion nozzle, and the fluorine stream half width, w , and F, DF mole fractions, X_F, X_{DF} . These eight quantities are constrained by i) an optimal cavity performance criterion, ii) the continuity equation, and iii)-v) combustor equilibrium, mass and energy balances. Also, vi) the characteristic temperature for cavity flow is determined mainly by X_F . Maximum power occurs at minimum w^* . With $X_F = 0.1$, $w^* \approx 0.01$ cm, and mixing by laminar diffusion between H_2 and F (dilute in He) streams, the maximum required combustor temperature would be about 1240K. Much larger F-atom mole fractions would produce thermal choking ("thermal blockage") in the supersonic flow, but $T_0 \leq 1300$ K at $X_F = 0.20$.

may be of interest. Corrosion of uncooled laser nozzles may be prevented if the construction material forms an involatile passivating fluoride coating. Due to rapid convective mass transfer at the nozzle throat, evaporation of a passivating fluoride would occur at nearly its vacuum sublimation rate. Evaporation from a nozzle passivated by the least volatile fluorides (CaF_2 , SrF_2 , and rare-earth trifluorides) would yield a 10% increase in w^* (initially 0.01 cm) in about 1 hour at 1300K.

Discussion - This paper shows that materials resistant to fluorine at temperatures up to ca. 1300K are of primary importance in the development of HFSDL's and that useful fluorine resistance at the throat of a laser nozzle will not be found with passivating metal fluorides unless the vacuum evaporation coefficient, α , of the fluoride is small. For LaF_3 , $\alpha = 1.0$; most other candidate fluorides have not been studied.

The conclusion that a passivating fluoride would evaporate from a laser nozzle throat at nearly its vacuum sublimation rate is based on the rates of transport of F-atoms to the surface of a cooled/laser nozzle computed by Ferrell, Kendall, and Tong (16).

Figure 1 shows our calculation of the combustor temperature - pressure relation, assuming adiabatic combustion of a D_2 - excess F_2 mixture whose initial temperature is 298K. The lines indicate the P_0 (T_0) relations for different X_{F} at which the fraction of total fluorine present as atomic fluorine equals 95% of its maximum possible value. This slight derating of combustor F-atom yield permits a substantial reduction in combustor temperature (ca. 100K).

Research to date has been guided by the belief that much higher temperatures would be of interest. Thus, a number of interesting candidate materials for HFSDL's have been rejected, but may yet find useful applications. Some of these are i) the heavier rare earth metals, whose melting points exceed 1500K and whose fluorides melt above 1400K. (However, see Section VIII for the F/Gd reaction kinetics; ii) yttrium metal or yttrium compounds, whose fluoride shatters when cooled through its phase transition temperature (14) (1350K); iii) MgO, which forms a MgO/MgF_2 eutectic at 1485K and exhibits fluoride film protection (61) to ca. 1360K.

Table I presents the vapor pressures of the least volatile fluorides. In many cases, these data were obtained by extrapolating measured results outside the range of measurement, and are, therefore, somewhat uncertain.

The melting points of the rare-earth metals and their trifluorides are illustrated in Fig. 2. The melting points of the heavier rare earth metals are sufficient for use as HF laser construction metals. However, we find (see Section VIII) that the fluorination of Gd to form solid GdF_3 is not a passivated process.

III. AERODYNAMIC LEVITATION OF LASER HEATED SOLIDS IN GAS JETS (62)

Abstract - Solid spheres were aerodynamically levitated in gas jets and laser heated to temperatures above 2000 K. Stable levitation in a supersonic jet from a 0.081 cm nozzle was demonstrated with 0.03 to 0.20 gram, 0.24 - 0.47 cm diameter specimens at a height between 0.7 - 2.0 cm above the nozzle and ambient pressures between 1.1 - 19 torr. An empirical model of supersonic jet levitation accurately predicts height vs. pressure over the full range of conditions that were investigated. The efficiency with which jet momentum is converted into levitation force decreases with the jet:specimen diameter ratio and the jet Reynolds number. The rate of jet spreading with distance from the nozzle deduced from levitation experiments agrees with that measured by pitot tube traverses of the jet. Pitot tube pressure measurements also reveal a transition from laminar to turbulent supersonic jet flow at a jet Reynolds number (ca. 1300) just above the maximum value at which stable levitation is observed. Laser heating reduces the jet momentum required for levitation at a given height and increases levitation stability. In experiments with subsonic jets, the required jet momentum flow rate exceeds the specimen weight by ca. $2/C_D$ where C_D is the specimen drag coefficient at its terminal free fall speed under the ambient conditions. Exploratory studies of laser heated liquid levitation were unsuccessful.

Discussion - This technique was used for the F/LaB₆ kinetic study (See Section IX). Specimen mass measurements before and after reaction with fluorine or fluoride coating evaporation yield the flux of molecules produced by reaction to ca. 10^{-14} cm² sec⁻¹ or the effective thickness of a passivating coating to ca. 10^{-5} cm. The apparatus is illustrated in Fig. 3.

IV. KINETICS OF THE F/ALUMINA GASIFICATION REACTION (38)

Abstract - Intrinsic kinetics for the F/alumina gasification reaction were measured using a low pressure, transonic microwave discharge flow reactor technique, at $p_F = 2.4$ Pa and $1100 < T < 2000$ K. Rate measurements were obtained on polycrystalline alumina tubes or single crystal sapphire rods which were heated with a CW CO₂ laser and on alumina tubes heated internally by a tungsten filament electrical heating element.

Impurities greatly influence the rate of reaction, which is negligible below 1500K for uniformly heated specimens containing less than 1% Ca. The impurities diffuse from higher to lower temperature regions of specimens that are not uniformly heated. The F-atom reaction probability on pure alumina or sapphire at $T > 1100$ K exceeds 0.5.

V. SPECTRAL EMITTANCE OF POLYCRYSTALLINE ALUMINA (39)

Abstract - The spectral emittance of polycrystalline alumina was measured at $T = 1660, 1830$ K. for $0.37 \mu < \lambda < 0.85 \mu$, and at $\lambda = 0.66 \mu$, between 1400-2100K. These measurements were obtained on 0.15cm diameter rods which were heated, in air, by a CW CO₂ laser. Emittances were obtained by alternately focusing an image of

the rod and of a black body hole in the rod onto the entrance aperture of a monochromator or by measuring the surface and black body temperatures with an optical pyrometer. The spectral emittance of alumina increases with temperature and is given, at 0.66μ , to ca. $\pm 5\%$ by the expression $\epsilon_{0.66} = 3.6 \times 10^{-4} T$. At constant temperature ϵ decreases with an increase of wavelength between $0.37-0.6\mu$ and is nearly constant between $0.6-0.85\mu$. These and other data show the emittance of polycrystalline alumina is larger and the transmittance smaller than values estimated from specimen grain size and the absorbance, transmittance of sapphire crystal. A (weak) surface absorption process is suggested to explain this difference in the optical properties of single crystal and polycrystalline aluminum oxide.

VI. KINETICS OF THE F_2/B_4C REACTION

Abstract - Intrinsic kinetics for the F_2/B_4C reactions were measured using a low pressure, duct flow reactor technique. F-atom reaction was studied by use of a microwave discharge to dissociate F_2 . Rate measurements were obtained from mass loss of a short B_4C duct through which the reactant flowed. The F/B_4C reaction probability $P(F_2)$ at $P(F_2) = 4.6 - 14$ Pa depends only on temperature and increases from 2×10^{-3} at 570K to 0.35 at 1000K. The F_2/B_4C increases from 4×10^{-3} at 740K to 0.07 at 1000K.

Discussion - This study presents the kinetics of fluorine reaction with one of two phases in the La - B - C system (32) that can coexist with a mixture of LaB_6 and carbon (see Fig. 4). Reaction of fluorine with the second phase, LaB_6C_2 , has not been investigated but the F/carbon reaction has been studied (2, 52) in much detail. The kinetic data for F/B_4C reaction are presented in Fig. 5. The reaction probability is the fraction of F-atoms or F_2 -molecules striking the B_4C surface which react to form BF_3 and CF_4 product molecules.

VII. KINETICS OF THE F/Re GASIFICATION REACTION

The F/Re gasification kinetics have been measured by methods described elsewhere (1, 7) to obtain the results illustrated in Figure 6. The figure plots the logarithm of the rhenium gasification probability, defined as the rhenium removal : fluorine atom impingement flux ratio versus reciprocal temperature. Since the product of reaction is ReF_4 (58), the F-atom reaction probability is 4 times greater than the rhenium gasification probability and the rate of reaction in the high temperature range where rate decreases with temperature is expected to increase with the 4-th power of the F-atom partial pressure. Rate measurements at $P_F = 0.0023, 0.0048, \text{ and } 0.0086$ torr confirm this conclusion. It is apparent that rhenium displays no useful fluorine resistance at high temperature, except above ca. 1600K when the fluorine pressure is very small. These results agree with the expected kinetic behavior suggested by the trends among other third-row transition metal fluorine reactions (1), which are illustrated in Figure 7.

VIII. HIGH TEMPERATURE KINETICS OF THE F/Gd REACTION

Gadolinium metal melts above 1600K (26), and its fluoride is involatile (11) and melts above 1500K (15). If it formed a passivating fluoride coat, gadolinium metal would be an interesting fluorine resistant material, especially

since it is stable in the atmosphere, easy to fabricate, and relatively inexpensive. A second reason for investigating the Gd/F reaction is to evaluate the effect of a large substrate metal activity on the passivating nature of rare-earth metal fluoride coatings.

The Gd/F reaction rate was studied by measuring the electrical resistance vs time of electrically heated Gd ribbon in atomic fluorine at temperatures ca. 1100-1500K. The rate of reaction is rapid, proportional to fluorine pressure, nearly independent of temperature, and independent of time, even after a fluoride coat, greater than 50 micron thick has formed. Thus, Gd metal is not a good fluorine resistant material because the fluoride coat formed on it is not passivating. The fluoride coat has a gray-black color, unlike GdF_3 , suggesting that the solubility of Gd in GdF_3 is substantial at high temperatures and unit metal activity. These observations imply that high metal activities are not conducive to formation of thin passivating fluoride coats, because rapid metal diffusion through the coating produces rapid reaction with fluorine at the fluoride-fluorine interface.

IX. HIGH TEMPERATURE KINETICS OF FLUORINE REACTION WITH LaB_6

LaB_6 reacts with atomic fluorine to form a passivating, white LaF_3 coating. Further reaction then proceeds at the coating evaporation rate which can be calculated from the vapor pressure of LaF_3 (35, 40) and the prevailing gas phase mass transfer coefficient. Rate data at $p(F) = 0.12$ torr are given in Fig. 8.

The LaF_3 coating thickness required to passivate F/ LaB_6 reaction is large for i) porous LaB_6 specimens, ii) sample LaB_6 -2, of low porosity (0.7%) and density equal to 4.68 g/cm³ (99.3% of theoretical density), or iii) LaB_6/C and $LaB_6/MoSi_2$ composites. Thin LaF_3 coatings (less than 3 mg/cm², or about 5 microns₃ at $p(F) = 0.12$ torr) occur on sample LaB_6 -4, of low porosity (0.7%) and 4.59 g/cm³ density (97.5% of theoretical density).

The LaB_6 phase exists over a considerable composition range (21, 22) as a result of La vacancy formation. The lattice parameter is essentially independent of composition. Therefore, the density measurements on LaB_6 samples which form a thin passivating LaF_3 coating in fluorine imply that the composition is actually $La_{0.96}B_6$ (or $LaB_{6.22}$). The lanthanum activity in this material would then be smaller by several orders of magnitude than it is in the more dense nearly stoichiometric substance (23).

The facts that thick LaF_3 coatings occur on nearly stoichiometric LaB_6 ($a_{La} = 10^{-2}$) and on gadolinium metal ($a_{Gd} = 1$), but not on La deficient LaB_6 , imply that the coating growth process occurs by diffusion of dissolved La through the coating. Then LaF_3 coating thickness should not increase much with fluorine pressure.

LaF_3 coating thickness has been measured on LaB_6 specimens exposed to atmospheric pressure fluorine-rich H_2/F_2 flames (17, 18, 34, 36, 52, 59, 60). The material which gave thicker coatings (ca. 30 microns, or 18 mg/cm²) at $p(F) = 0.12$ torr produced a 100 micron thick coating in the flame tests (34). This relatively small change over a thousand-fold change in the F-atom pressure

supports the postulate that coating thickness depends on substrate lanthanum activity. However, flame test results are not available on the specimens that are passivated by thin LaF_3 coatings.

Figure 9 reports our coating mass measurements, which may be converted to an effective coating thickness via the density of LaF_3 , 5.9 g/cm^3 . The figure presents coating mass per unit area as a measure of coating thickness. Specimen area is taken as the area of a sphere of equal mass and does not include corrections for surface roughness. The results of three experiments with sample LaB_6 -2 (open symbols) and two experiments with sample LaB_6 -4 (filled symbols) are given. The figure plots $\text{LaF}_3(s)$ mass per unit area after reaction for 20-50 minutes at the indicated temperatures, and $P_F = 1.6 \times 10^{-4} \text{ atm}$. The abscissa is the number of times that the coating has been formed on the specimen. Evaporation of the coating at $T = 1500\text{K}$ was carried out between each run.

Further details of our F/LaB_6 work are given in Reference 61.

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Table 1
Melting Points, Transition Temperatures, and Vapor Pressures of Refractory Fluorides

| Fluoride | T _m (K) | T _t (K) | Vapor pressure, atm | | T _m | Refs. |
|------------------|--------------------|--------------------|---------------------|----------|----------------|----------|
| | | | 1400K | 1500K | | |
| MgF ₂ | 1536 | | 6.71E-6 | 5.55E-5 | 1.11E-4 | 9 |
| CaF ₂ | 1691 | 1424 | 2.73E-7 | 2.57E-6 | 1.81E-5 | 9 |
| BaF ₂ | 1563 | | 5.03E-6 | 3.89E-5 | 1.22E-4 | 9 |
| SrF ₂ | 1673 | | 5.64E-7 | 4.75E-6 | 3.00E-5 | 9 |
| LaF ₃ | 1766 | | 9.14E-7 | 9.63E-6 | 7.56E-5 | 11,14 |
| PrF ₃ | 1668 | | 1.87E-6 | 1.88E-5 | 1.42E-4 | 11,14 |
| NdF ₃ | 1647 | | 1.56E-6 | 1.64E-5 | 1.28E-4 | 11,14 |
| SmF ₃ | 1573 | 763 | 5.29E-6 | 5.38E-5 | 2.43E-4 | 11,15,40 |
| GdF ₃ | 1505 | 1348 | 5.56E-7 | 6.39E-6 | 7.15E-6 | 11,15 |
| DyF ₃ | 1430 | 1305 | 8.42E-7 | | 1.79E-6 | 11,15 |
| ErF ₃ | 1419 | 1390 | 7.53E-7 | | 1.18E-6 | 11,15 |
| ScF ₃ | 1825 | | 3.86E-5 | (3.24E4) | (2.08E-3) | 11,15 |
| YF ₃ | 1428 | 1350 | 1.45E-6 | | 2.94E-6 | 12,14 |

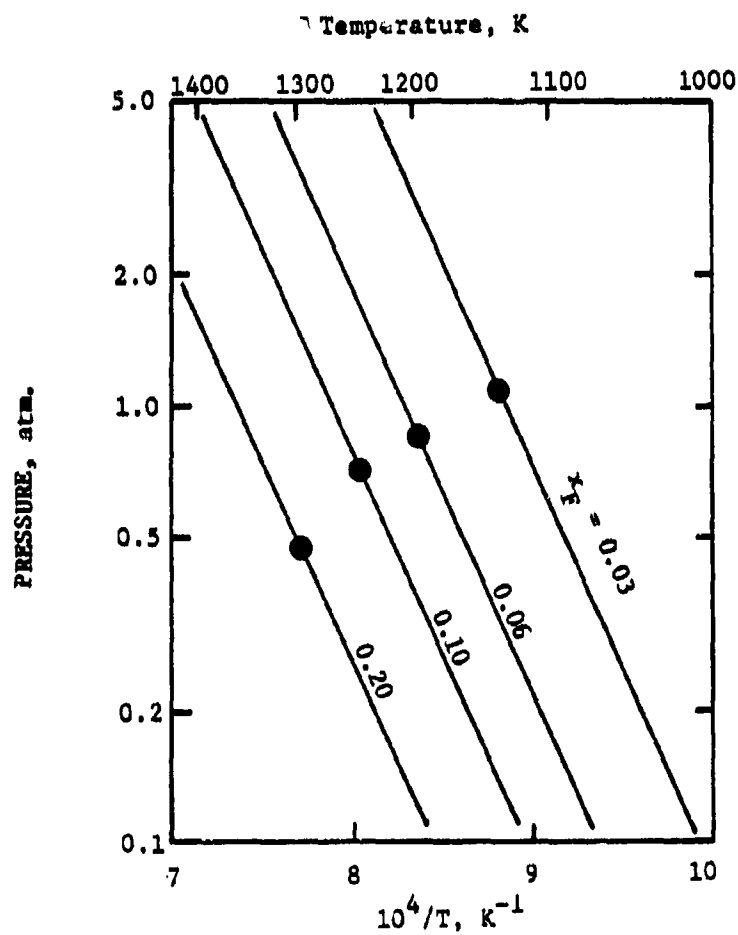


Figure 1. $F_2/H_2/He$ adiabatic combustor temperature and pressure at $\eta_c = 0.95 \cdot \eta_c(\max)$.

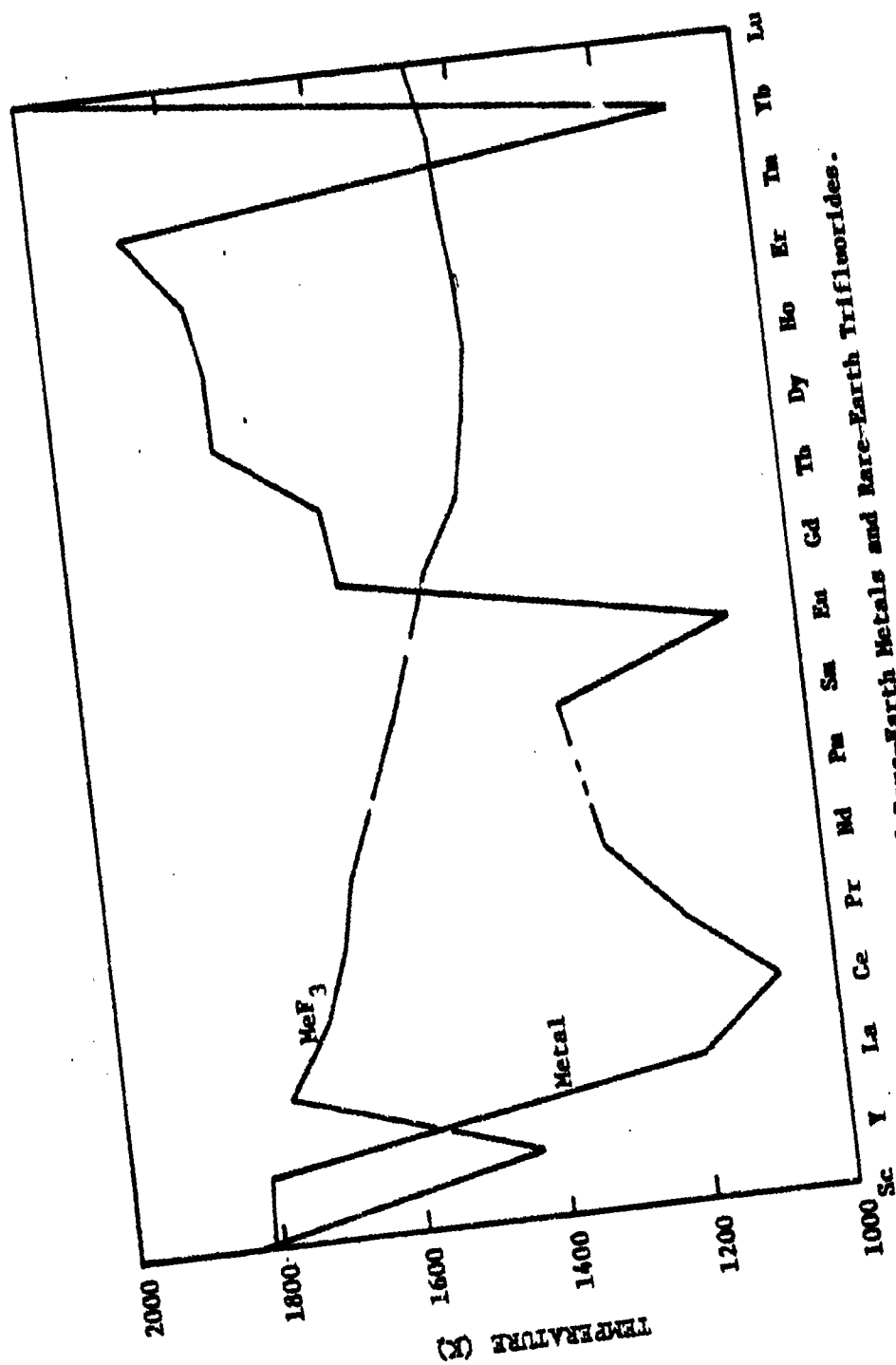


Figure 2. Melting Points of Rare-Earth Metals and Rare-Earth Trifluorides.

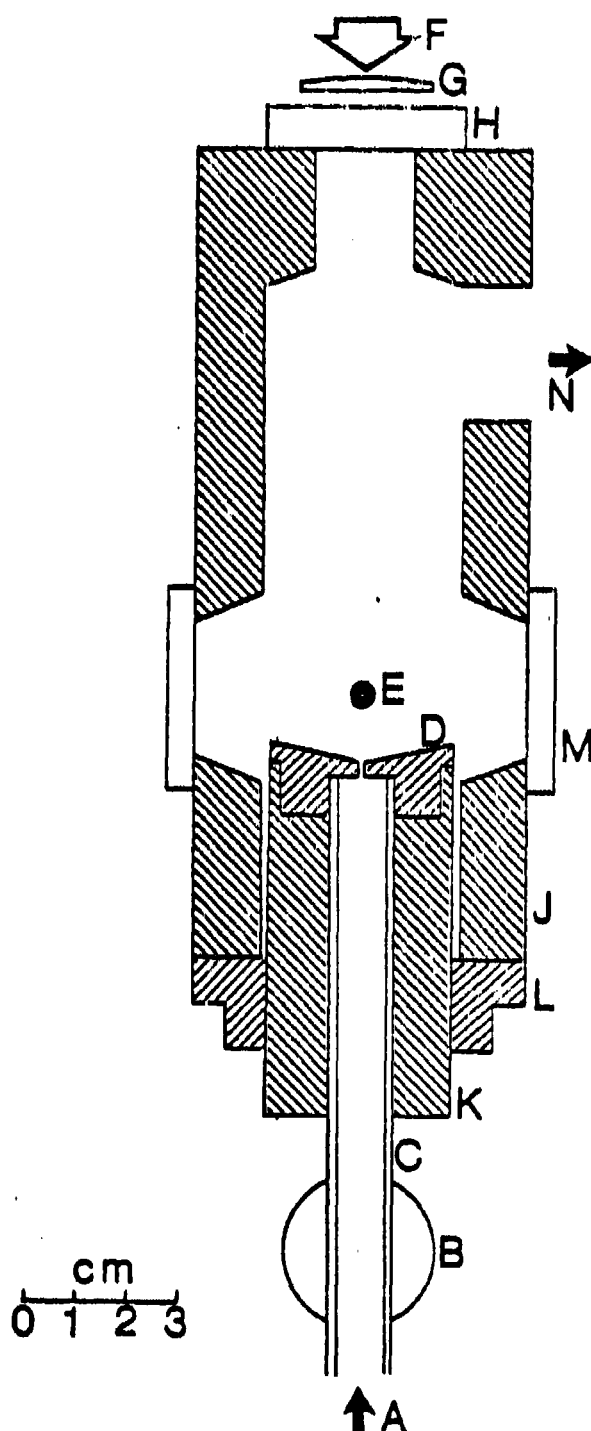


Figure 3. Aerodynamic Levitation Flow Reactor, A- Reactant gas flow (Ar/F_2 mixture); B- 2450 MHz, 80 watt microwave discharge; C- Alumina discharge tube; D-Anodized aluminum nozzle; E-Aerodynamically levitated specimen; F- CW CO_2 laser beam; G- ZnSe lens (optional); H- NaCl window; J- Water-cooled aluminum housing; K- Water-cooled nozzle support; L- O-Ring coupling; M- Pyrex windows for optical pyrometer and sensor for laser power controller; N- to manometer, throttle valve, trap, and vacuum pump.

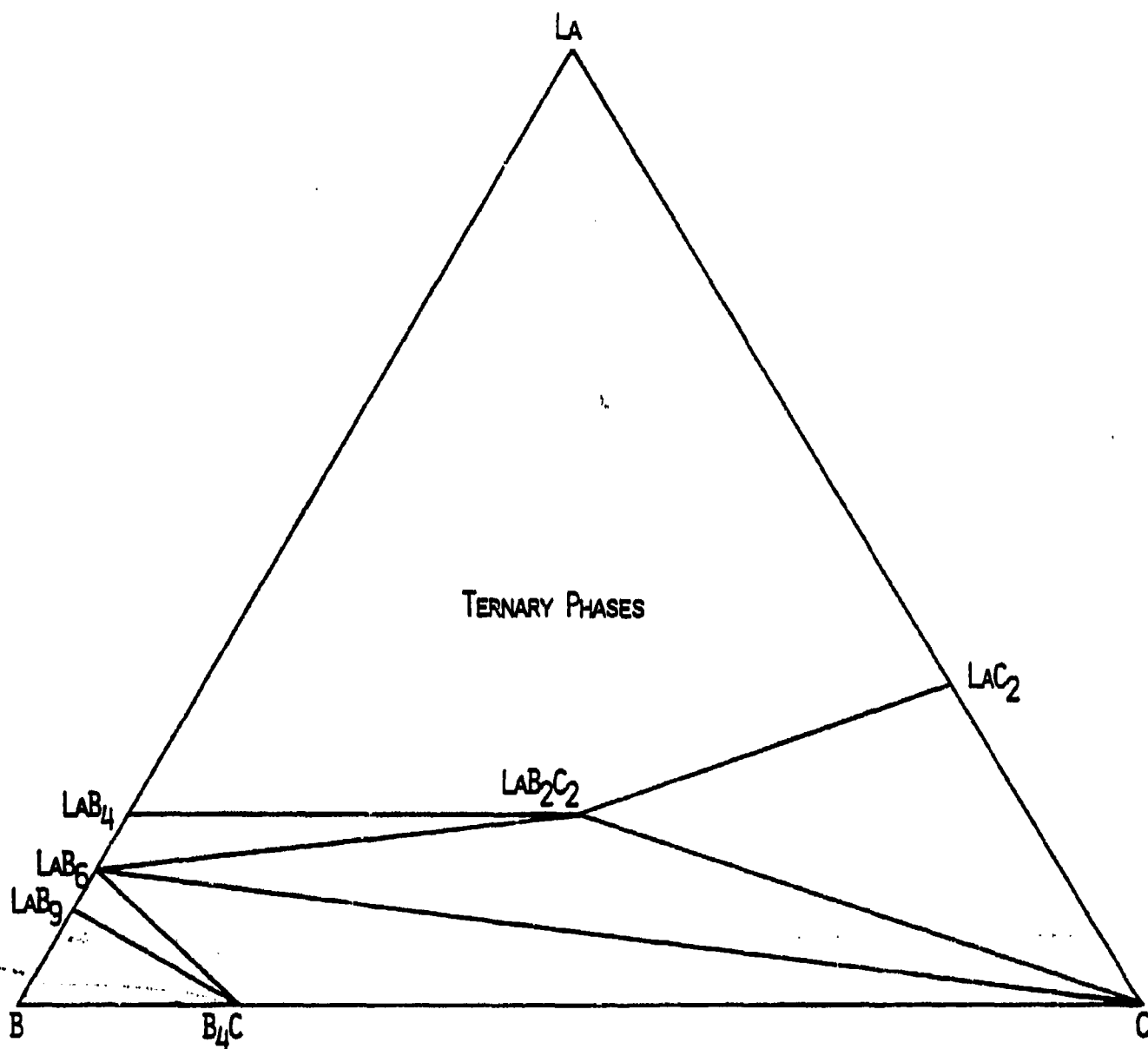


FIGURE 4. LANTHANUM-BORON-CARBON TERNARY PHASE DIAGRAM.

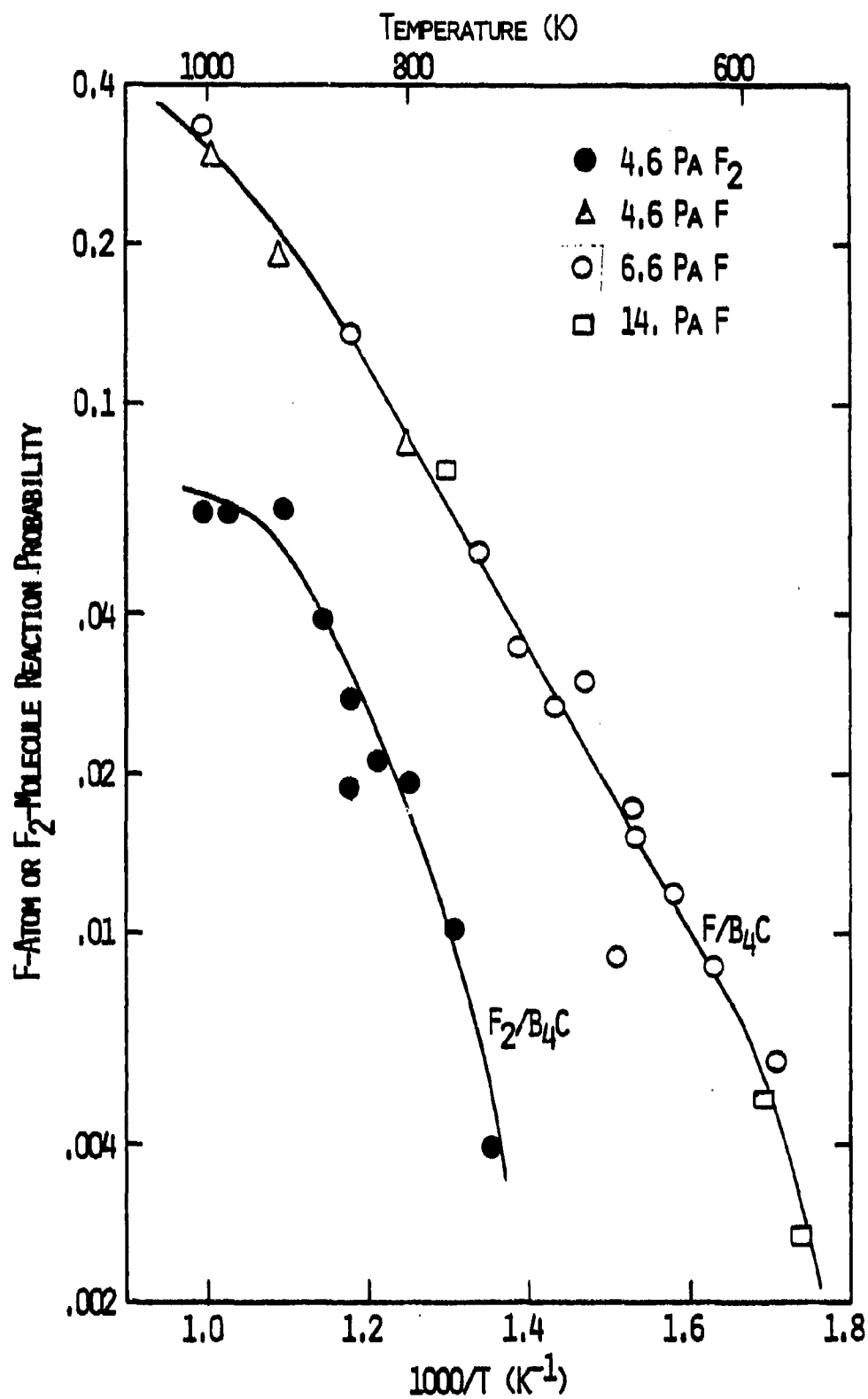


FIGURE 5. F, F₂/B₄C GASIFICATION KINETICS.

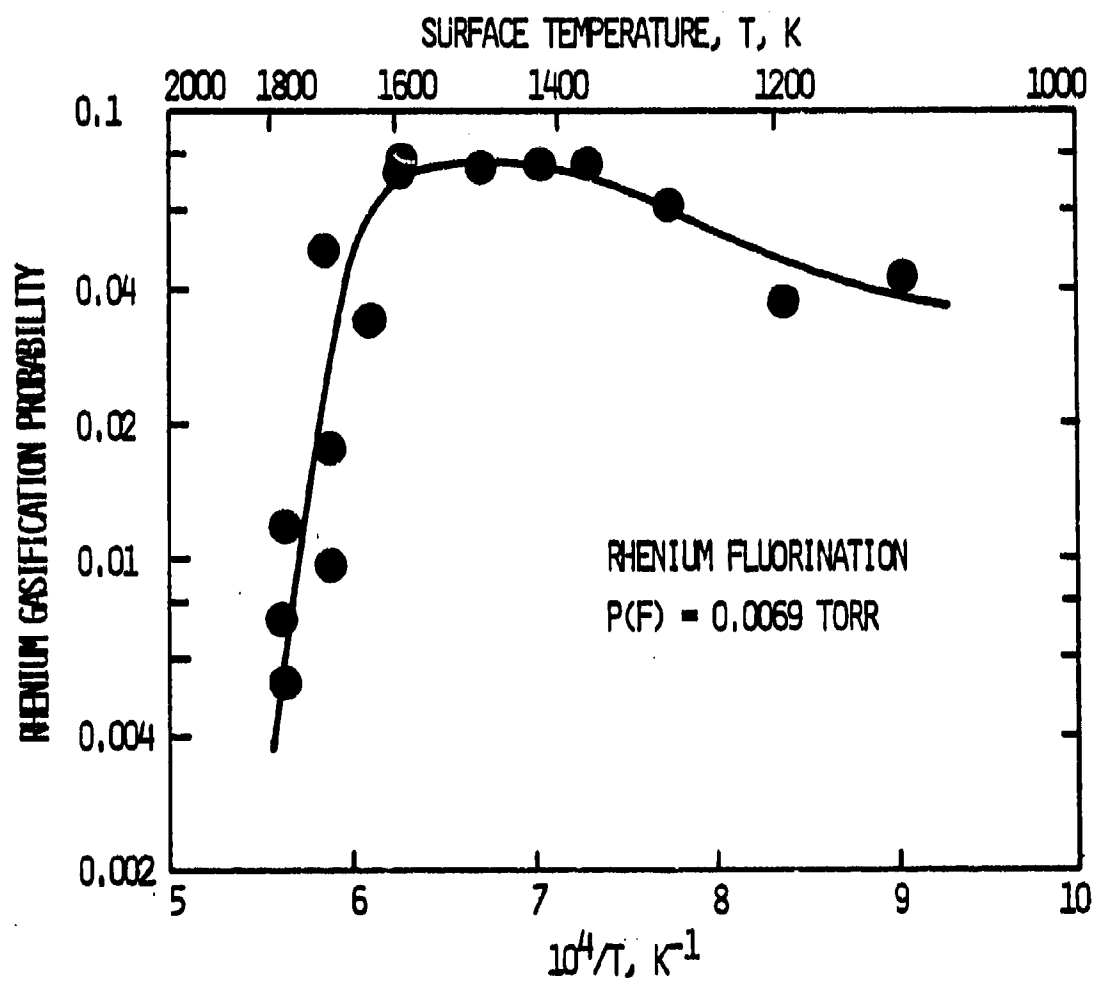


Figure 6. Rhenium fluorination kinetics.

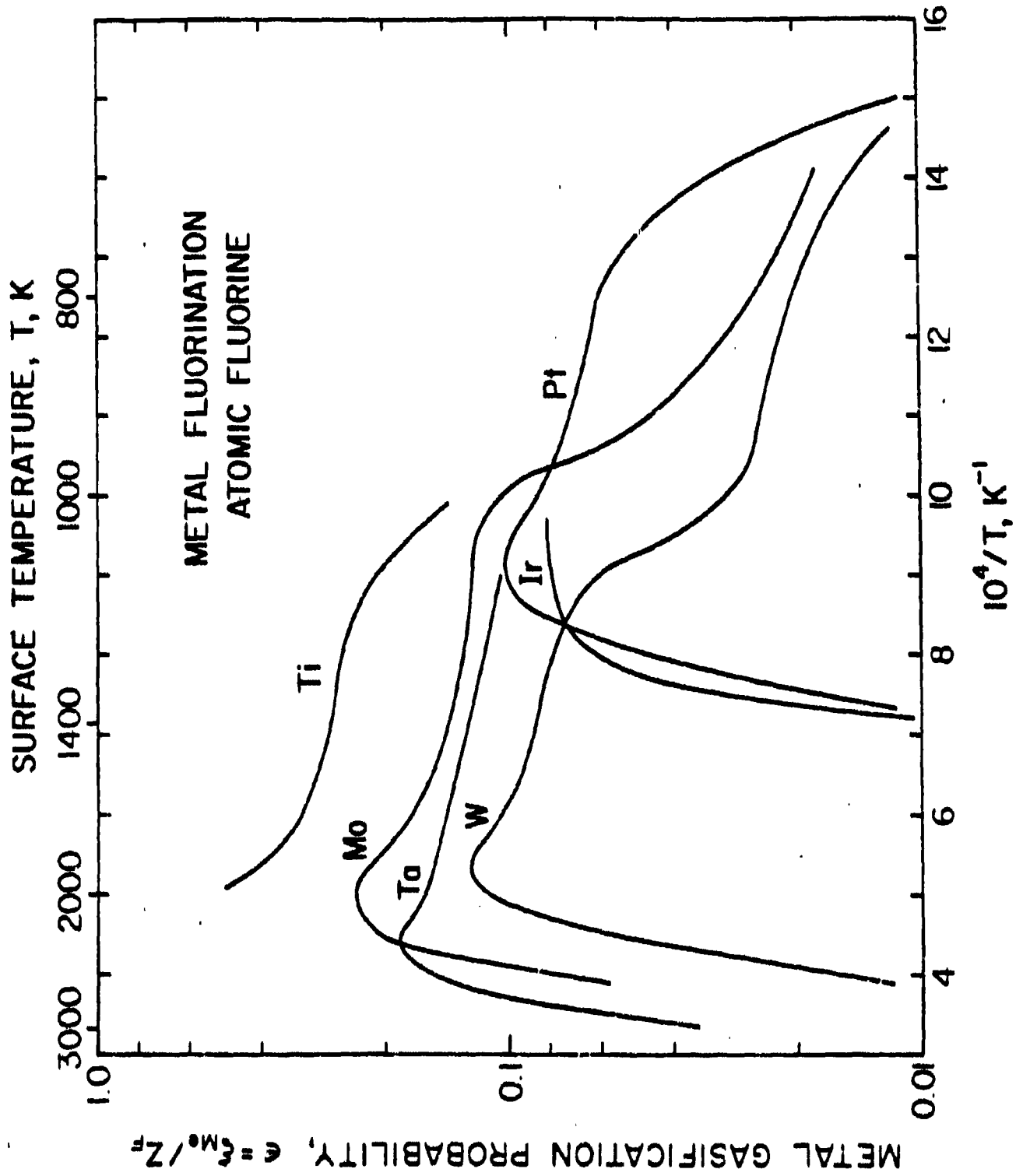


Figure 7. Transition metal fluorination kinetics.

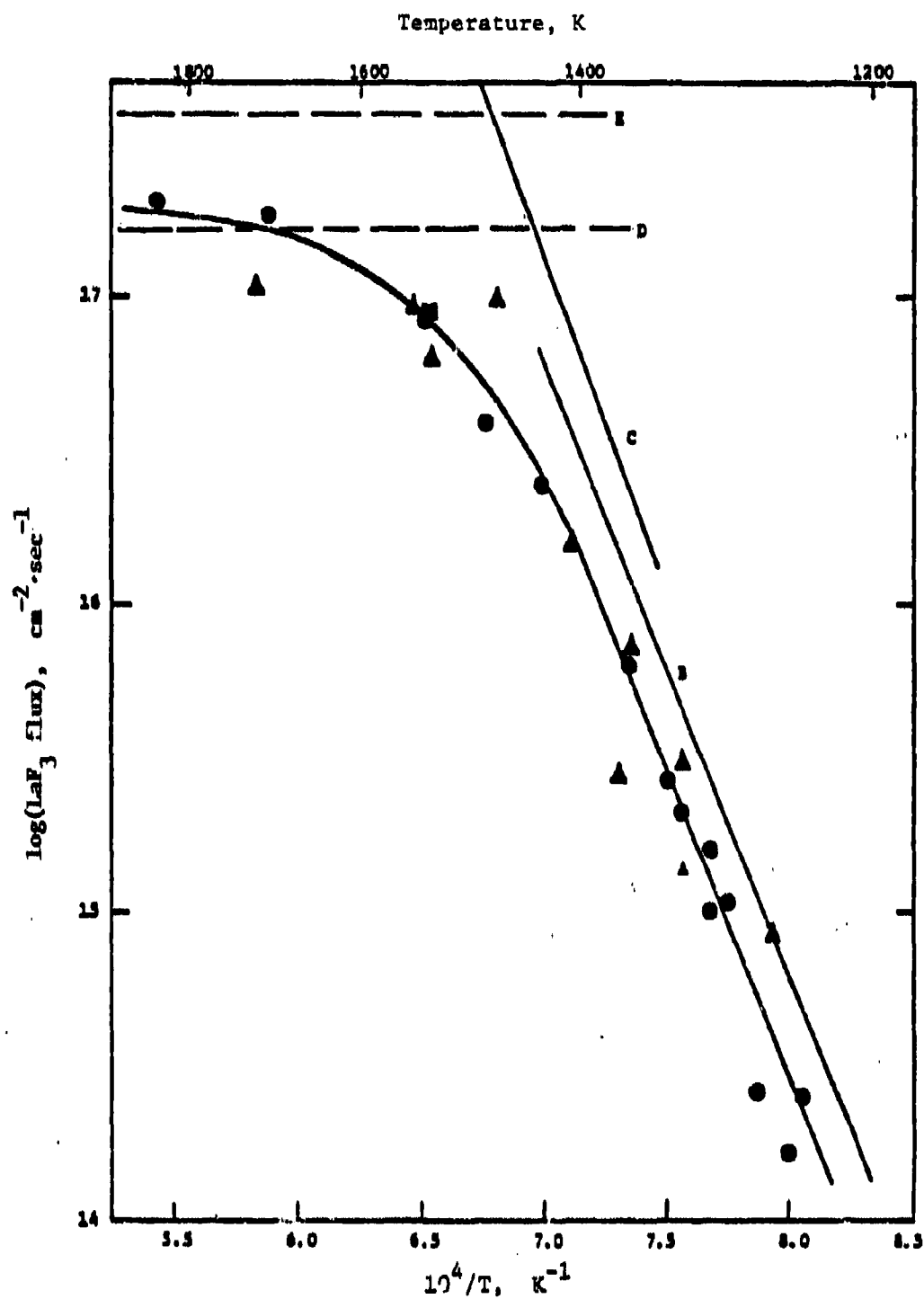


Figure 8. LaB_6/F reaction kinetics.

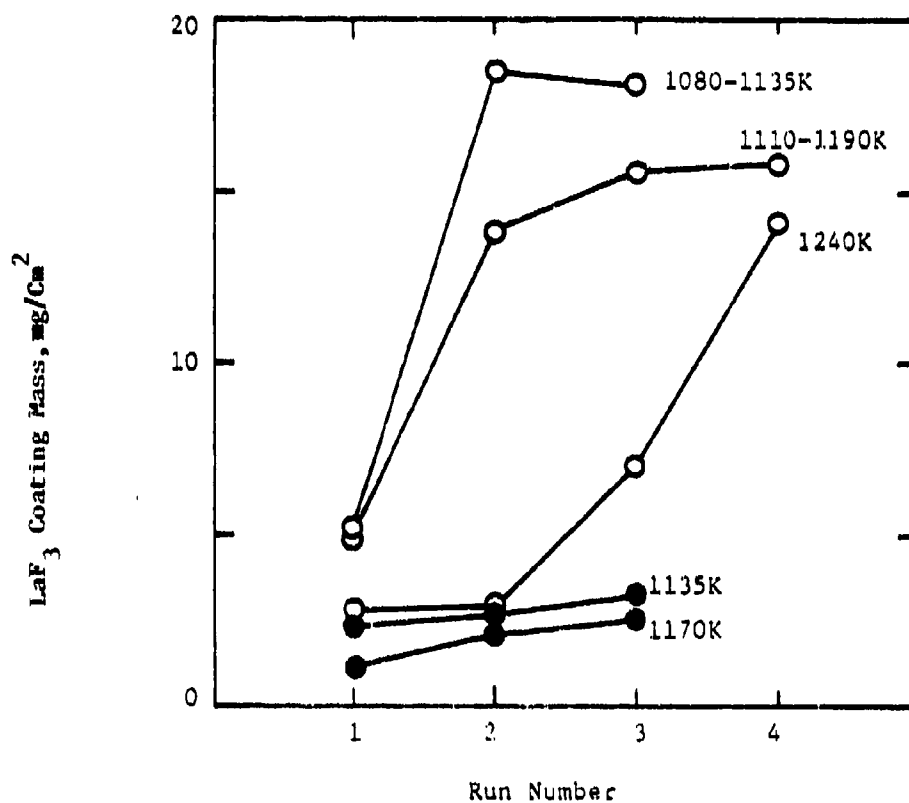


Figure 9. LaF₃ coating mass measurements.

Open symbols - LaB₆-2.

Filled symbols - LaB₆-4.